

# Magnetic Properties of Condensed Aromatic Hydrocarbons with Four Benzene Nuclei. I. On the Diamagnetism of Chrysene

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## Introduction

The Pascal's additive law<sup>(1)</sup> of magnetic susceptibility is very well adopted to the aliphatic compounds but the values of molecular susceptibility of aromatic compounds in the treatment as well as the aliphatic compounds for the carbon and hydrogen atoms are diamagnetically smaller than the experimental values. Pascal assigned this excessive parts of diamagnetism to the respective carbon atoms that form the condensed nuclei. Taking into account the constitutive corrections the larger the condensibility of benzene nuclei is, the larger the difference between the calculated values by additive law and the experimental ones becomes.

On the other hand, F. London<sup>(2)</sup> calculated the ratios of the diamagnetic anisotropies of various condensed aromatic compounds to that of benzene by a quantum mechanical procedure, based on Hückel's molecular orbital treatment, extending to the case of the presence of a magnetic field and obtained an excellent agreement with experiment.

In general, the diamagnetism of condensed aromatic hydrocarbons becomes larger with the increase of hexagon number, but it will be expected that the diamagnetic susceptibilities of condensed aromatic hydrocarbons with the same number of hexagon are changed by the form of molecule. Accordingly, the London's theory is applied to the theoretical calculation of the anisotropic part in the condensed aromatic hydrocarbons with four benzene nuclei and the experimental values are compared.

## Form of Chrysene Molecule

The X-ray analysis of chrysene crystal has been made by Iball<sup>(3)</sup>. The crystal belongs to

the space group  $C_{2h}^6$  (12/C) or  $C_3^4$  (1C). The dimensions of the unit cell are  $a=6.59$ ,  $b=7.84$ ,  $c=14.17$  Å,  $\beta=103.5^\circ$ , and it contains 4 molecules. The crystal density 1.27, melting point  $250^\circ\text{C}$ ., boiling point  $448^\circ\text{C}$ ., molecular weight 228, and the form of molecule is plane and consists of regular hexagons with inter-atomic distances of 1.41 Å.

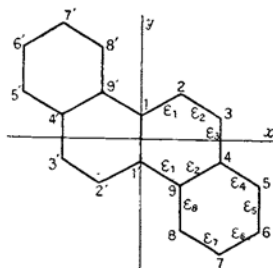


Fig. 1.

## Theoretical Calculation

The present calculation follows the same notation and procedure as London's paper.<sup>(4)</sup> London's secular equation is as follows:

$$|\eta_{kl} \exp(2\pi i f_{kl}) - x \delta_{kl}| = 0, \quad (1)$$

where  $\eta_{kl} = \begin{cases} 1 & \text{if } k \text{ is a neighbor of } l \\ 0 & \text{if } k \text{ is not a neighbor of } l \end{cases}$   
 $\delta_{kl} = \begin{cases} 1 & \text{if } k=l \\ 0 & \text{if } k \neq l, \end{cases}$

$$f_{kl} = \frac{e}{2hc} H(x_k y_l - x_l y_k), \quad (2)$$

$$\exp(2\pi i f_{kl}) = W_{kl}/W_1, \quad (3)$$

$$\text{and} \quad x = \frac{E^{(1)} - W_0}{W_1} \quad (4)$$

In Eq. (2),  $H$  is the field strength,  $x_k$  etc. are the coordinates and  $f_{kl}$  can be considered as a numerical value proportional to the magnetic flux through the area of the triangle

(1) Cf., for instance, P. W. Selwood, "Magnetochemistry", New York, 1943.

(2) F. London, *J. de Physique*, **8**, 397 (1937).

(3) J. Iball and J. M. Robertson, *Nature*, **132**, 750 (1933); J. Iball, *Proc. Roy. Soc. (London)*, **A 146**, 140 (1934).

(4) F. London, *J. de Physique*, **8**, 397 (1937).

formed by the neighbors  $k, l$  and the origin, arbitrarily chosen in the plane of the molecule. In Eq. (3),  $W_{kl}$  represents the exchange integral in the presence of magnetic field and  $W_1$  is the ordinary exchange integral of the nearest neighbors of the orbital theory in the absence of magnetic field. In Eq. (4),  $E^{(1)}$  is the ordinary first order perturbation energy and  $W_0$  is the Coulomb integral independent of the magnetic field.

Following the above conditions and the model shown in Fig. 1, the following secular determinant of chrysene molecule can be gained.

$$\begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 1' & 2' & 3' & 4' & 5' & 6' & 7' & 8' & 9' \\ 1 & -x\varepsilon_1 & & & & & & & & & & & & & & & & \varepsilon_1^* \\ 2 & \varepsilon_1^* - x\varepsilon_2 & & & & & & & & & & & & & & & & \\ 3 & & \varepsilon_2^* - x\varepsilon_3 & & & & & & & & & & & & & & & \\ 4 & & & \varepsilon_3^* - x\varepsilon_4 & & & & & & & & & & & & & & \varepsilon_2 \\ 5 & & & & \varepsilon_4^* - x\varepsilon_5 & & & & & & & & & & & & & \\ 6 & & & & & \varepsilon_5^* - x\varepsilon_6 & & & & & & & & & & & & \\ 7 & & & & & & \varepsilon_6^* - x\varepsilon_7 & & & & & & & & & & & \\ 8 & & & & & & & \varepsilon_7^* - x\varepsilon_8 & & & & & & & & & & \\ 9 & & & & & & & & \varepsilon_8^* - x\varepsilon_1 & & & & & & & & & \\ 1' & 1 & & & & & & & \varepsilon_1^* - x\varepsilon_2 & & & & & & & & & \\ 2' & & 1 & & & & & & \varepsilon_2^* - x\varepsilon_3 & & & & & & & & & \\ 3' & & & 1 & & & & & \varepsilon_3^* - x\varepsilon_4 & & & & & & & & & \\ 4' & & & & 1 & & & & \varepsilon_4^* - x\varepsilon_5 & & & & & & & & & \\ 5' & & & & & 1 & & & \varepsilon_5^* - x\varepsilon_6 & & & & & & & & & \\ 6' & & & & & & 1 & & \varepsilon_6^* - x\varepsilon_7 & & & & & & & & & \\ 7' & & & & & & & 1 & \varepsilon_7^* - x\varepsilon_8 & & & & & & & & & \\ 8' & & & & & & & & & 1 & & & & & & & & \\ 9' & & & & & & & & & & 1 & & & & & & & \\ & & & & & & & & & & & \varepsilon_1 & & & & & & \\ & & & & & & & & & & & & \varepsilon_2^* & & & & & \\ & & & & & & & & & & & & & \varepsilon_8 - x & & & & \end{vmatrix} = 0, \quad (5)$$

where  $\varepsilon_k = \exp(2\pi i f_{k,k+1})$

and

and  $\varepsilon_k^* = \exp(-2\pi i f_{k,k+1})$ .

For convenience' sake,  $\varepsilon_k$  is preferred to  $\varepsilon_k^*$  in case of the clockwise rotation about the origin.

This secular determinant can be transformed to the type as follows:

$$\begin{vmatrix} \Delta_1 & 0 \\ 0 & \Delta_2 \end{vmatrix} = 0.$$

Therefore Eq. (5) can be separated into the solution of two determinants, namely

$$\Delta_1 = \begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 1 & (1-x)\varepsilon_1 & & & & & & & \varepsilon_1^* \\ 2 & \varepsilon_1^* - x\varepsilon_2 & & & & & & & \\ 3 & & \varepsilon_2^* - x\varepsilon_3 & & & & & & \\ 4 & & & \varepsilon_3^* - x\varepsilon_4 & & & & & \varepsilon_2 \\ 5 & & & & \varepsilon_4^* - x\varepsilon_5 & & & & \\ 6 & & & & & \varepsilon_5^* - x\varepsilon_6 & & & \\ 7 & & & & & & \varepsilon_6^* - x\varepsilon_7 & & \\ 8 & & & & & & & \varepsilon_7^* - x\varepsilon_8 & \\ 9 & \varepsilon_1 & & & & & & & \varepsilon_8 - x \end{vmatrix} = 0$$

and

$$\Delta_2 = \begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 1 & (-1-x)\varepsilon_1 & & & & & & & -\varepsilon_1^* \\ 2 & \varepsilon_1^* & -x\varepsilon_2 & & & & & & \\ 3 & & \varepsilon_2^* - x\varepsilon_3 & & & & & & \\ 4 & & & \varepsilon_3^* - x\varepsilon_4 & & & & & \varepsilon_2 \\ 5 & & & & \varepsilon_4^* - x\varepsilon_5 & & & & \\ 6 & & & & & \varepsilon_5^* - x\varepsilon_6 & & & \\ 7 & & & & & & \varepsilon_6^* - x\varepsilon_7 & & \\ 8 & & & & & & & \varepsilon_7^* - x\varepsilon_8 & \\ 9 & -\varepsilon_1 & & & & \varepsilon_2^* & & & \varepsilon_8 - x \end{vmatrix} = 0.$$

Expanding  $\Delta_1$  and  $\Delta_2$ , and after substitution of  $\varepsilon$  by  $f$ , we have

$$\begin{aligned} \Delta_1 = & x^9 - x^8 - 10x^7 + 8x^6 + 32x^5 - 21x^4 - 39x^3 \\ & + 22x^2 + 15x - 8 + (x^4 + x^3 - 4x^2 - 2x \\ & + 6)(2\pi f)^2 = 0 \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta_2 = & x^9 + x^8 - 10x^7 - 8x^6 + 32x^5 + 21x^4 - 39x^3 \\ & - 22x^2 + 15x + 8 - (x^4 - x^3 - 4x^2 + 2x \\ & + 6)(2\pi f)^2 = 0, \end{aligned} \quad (7)$$

where  $f = (e/hc) \cdot H \cdot S_B$ , (8)

$S_B$  = the area of each hexagon.

Since Eqs. (6) and (7) have the form:

$$F_1(x) + F_2(x) \cdot (2\pi f)^2 = 0 \quad (9)$$

and  $f$  is very small, the second term may be considered as a correction. Accordingly, let  $x'$  be a root of  $F_1(x) = 0$  and

$$x = x' + x''(2\pi f)^2 \quad (10)$$

be a root of Eq. (9),  $x''$  will be expressed approximately by

$$x'' = \frac{F_2(x')}{F_1'(x')} \quad (11)$$

according to Newton's equation. In Eq. (11),

$F_1'$  represents the first differential of  $F_1$  with regard to  $x$ .

Now we need nine roots of lower energy levels in eighteen roots of Eqs. (6) and (7). These values are shown in Table 1.

Table 1

$-x'$	$x''$
2.49904	+0.03965
2.16651	-0.00899
1.70076	-0.12892
1.53977	+0.06547
1.28577	+0.16687
1.21644	-0.29292
0.87532	+0.35968
0.79233	-0.58089
0.52013	+0.62639
$\Sigma; +0.24638$	

Substituting the values of  $x$  in Eq. (4),  $E^{(1)}$  is given and a susceptibility contribution of a  $\pi$ -electron becomes

$$\chi_p = - \left( \frac{\partial^2 E^{(1)}}{\partial H^2} \right)_{H \rightarrow 0} \quad (12)$$

From (4), (8), (10), (12) and numerical value of  $\Sigma(x'')$  we obtain the diamagnetic anisotropy of chrysene as follows:

$$\begin{aligned} \Delta\chi &= 2 \sum_{p=-\frac{N-2}{4}}^{\frac{N-2}{4}} \chi_p = -4 \Sigma(x'') |W_1| \left( \frac{2\pi e S_B}{hc} \right)^2 \\ &= 18 \Sigma(x'') \Delta\chi_{\text{Benz.}} \\ &= 4.43 \Delta\chi_{\text{Benz.}} \end{aligned} \quad (13)$$

where  $\Delta\chi_{\text{Benz.}}$  is the anisotropic contribution of  $\pi$ -electrons in benzene.

### Magnetic Measurements and Discussion

The principal diamagnetic anisotropies along the three principal axes of chrysene single crystal have been measured by K. Lonsdale and K. S. Krishnan.<sup>(5)</sup> These values are as follows:

$$\begin{aligned} K_1 &= -88.0 \times 10^{-6}, \quad K_2 = -83.3 \times 10^{-6}, \\ K_3 &= -310.8 \times 10^{-6}, \end{aligned}$$

then the anisotropic part per mole becomes

$$\Delta\chi = 4.17 \cdot \Delta\chi_{\text{Benz.}} \quad (14)$$

We measured the mass susceptibility of powdered chrysene by the modified Gouy's method<sup>(6)</sup> and chose the purified water as standard. This chrysene specimen had been extracted from coal-tar and purified by several recrystallizations and sublimations. The results obtained as follows:

$$\chi_g = -0.731 \times 10^{-6}, \quad \chi_M = -166.67 \times 10^{-6},$$

where  $\chi_g$  and  $\chi_M$  denote the mass and mole susceptibilities respectively. Accordingly, we can deduce  $\Delta\chi$  as follows:

$$\Delta\chi = 4.10 \cdot \Delta\chi_{\text{Benz.}}, \quad (15)$$

using the modification of Pascal's additive law.<sup>(7)</sup>

This result (Eq. (15)) coincides closely with that of relation (Eq. (14)), and the result calculated according to London's theory (Eq. (13)) shows a relatively good agreement with the experiments.

The difference of  $K_1$  and  $K_2$  in chrysene is small but, in general, it is expected that the larger the discrepancy of molecular form from the circle is, the larger this difference becomes. Accordingly, the relative diamagnetic anisotropies to benzene under the assumption of  $K_1 = K_2$  will become uncertainly, then it may be doubtful to compare the values of experimental relative anisotropy to the theoretical values. These questions have to be discussed further in detail.

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(5) K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. (London)*, **A 156**, 597 (1936); K. Lonsdale, *Proc. Roy. Soc. (London)*, **A 159**, 149 (1937).

(6) Cf., for example, P. W. Selwood, "Magnetochemistry," New York (1943); G. Hazato and K. Aida, *Rep. Glass Research Institute, Tohoku Univ.*, No. 3 (1949).

(7) G. Hazato, *J. Chem. Soc. Japan*, **64**, 483 (1943); H. Shiba and G. Hazato, *This Bulletin*, **22**, 92 (1949).